The Biogeochemistry of Chromophoric Dissolved Organic Matter in Coastal Waters

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LONG-TERM GOALS

The long-term goal of this research is to better understand the biogeochemical cycling of dissolved organic matter (DOM) in coastal waters. Of particular interest is the fate of terrigenous and anthropogenic dissolved organic matter and their effects on marine systems.

SCIENTIFIC OBJECTIVES

1.) *Determine high resolution spatial and temporal variability of chromophoric dissolved orgnaic matter (CDOM) in coastal regions*.

By applying recent advances in *in situ* measurement and real-time sampling, the differentiation of sources, synoptic mapping of distributions, and predictions of transformations of CDOM will become possible. An understanding of this natural variability is necessary for knowledgeable sampling strategies and relating chemical properties to governing physical processes in high energy environments such as coastal seas. In addition, large spatial coverage over a wide range of estuarine systems will provide valuable data in developing remote sensing algorithms.

2.) *Determine the reactivity of DOM in estuaries*

By examining sources and sinks of colored and non-colored DOM along salinity gradients, estimates of water mass residence times can be converted to average reactivities for the various sources of DOM in coastal waters. Only through high resolution, highly sensitive measurements may the different reactivities of several sources of CDOM be determined simultaneously.

3.) *Relate the molecular level structure of DOM to the optical properties of CDOM*.

Detailed molecular level characterization of DOM isolates by ^{1}H NMR, Pyrolysis GCMS, and lignin analysis will supply valuable structural information to augment optical measurements of CDOM. In order to reliably predict the important photochemical, biological, and chemical processes governing CDOM, and hence its reactivity, the link between structure and optical properties must be defined.

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4.) *To address the long-standing question: How much seawater DOM is derived from terrigenous sources?*

Differentiation of sources with both optical and chemical characterization techniques will allow an estimate of DOC flux out of these four quite different estuaries into the open ocean [Meyers-Schulte and Hedges, 1986]. By understanding the processes governing this flux, an estimate for entire continental shelves can be made. Further, detailed understanding of the processes controlling the fate and distribution of DOM in coastal waters will allow detailed modeling of the fate of contaminants such as hydrophobic organic contaminants (i.e. PCBs, PAHs, pesticides) as well as certain metals (Hg, Pb, Ag, etc) that are known to be associated with terrestrial, especially urban organic matter.

APPROACH

Development and deployment of a new undulating. towed sensor system (ECOSoar) designed specifically for optical measurements of CDOM will allow high spatial resolution measurements in 4 major US estuaries (Boston Harbor/Massachusetts Bay, Chesapeake Bay, San Diego Bay, and San Francisco Bay). Discrete seawater samples will validate *in situ* measurements while large volume samples will be taken to characterize the various sources of CDOM. Optical measurements will include absorption spectra, fluorescence excitation-emission spectra, and time-resolved fluorescence spectra. Further analyses will include high-temperature combustion dissolved organic carbon, chlorophyll-a, and elemental analysis. CDOM characterization will rely on ^{1}H-NMR, direct temperature mass spectrometry, and pyrolysis mass spectrometry of the high molucular weight fraction of DOM isolated and concentrated by ultrafiltration (>1000 NMW). Bernie Gardner (physical oceanographer-UMassBoston) will be in charge of deployment of the CTD and towed vehicle as well as assist in the overall design of the sensor system and sampling plan. Doctoral candidate Steve Rudnick will assist in deploying the LIF system. A soon-to-be hired graduate student will be in charge of large volume sampling and HMW DOM characterization by ^{1}H-NMR and mass spectrometry. Discrete optical measurements and DOC analyses will be handled by graduate students Penny Vlahos and Yixian Zhang. I will be in charge of overseeing the project, organizing cruises, analyzing samples and data, and disseminating the results.

WORK COMPLETED

Initial research into developing a towed vehicle to deploy the optical instrumentation mentioned above has led to the purchase of the Chelsea Instruments Nu-Shuttle. Initial testing will begin as soon as the vehicle arrives. A gas chromatography/mass spectrometer and a lifetime spectrofluorometer have also been purchased with installation of the GCMS completed and the spectrofluorometer arriving soon. The laser-induced fluorescence (LIF) system has been upgraded and is ready for deployment. It can be shipped anywhere and set up within two hours.

RESULTS

The major results so far are simply the purchase and installation of equipment that will be necessary for carrying out the proposed research. After discussion with several

undulating vehicle researchers, it appears that while the development of an undulating system is challenging, the system should come together fairly quickly and shows a great deal of promise. Our system will be the first of its kind, designed specifically for shallow coastal waters, capable of carrying a large payload, and integrating a pumping system for continuous sampling.

IMPACT/APPLICATION

High resolution optical measurements will allow a much better understanding of complex coastal processes. With a significant groundtruthing effort, this research should yield a new, powerful technique for examining episodic and small scale events and features in coastal waters.

TRANSITIONS

New instrumentation and the ECOShuttle will allow us to further examine coastal waters in other areas. An understanding that terrestrial systems do not have a large effect on offshore waters and that estuaries are great reactors for DOM is emerging. This project should support these new ideas with data from four major estuaries. Ongoing discussions with Paul Fucile and Frank Bahr (WHOI) and Burke Hales (Lamont-Doherty) involving the development of a coastal water undulating vehicle should have an impact on researchers interested in developing similar systems.

RELATED PROJECTS

1.) Bernie Gardner, doctoral candidate Steve Rudnick (UMassBoston) and I are completing an MIT SeaGrant funded study of Boston Harbor. We developed and deployed the LIF system in Boston Harbor on 10 cruises and are studying the spatial and temporal trends of DOM and polycyclic aromatic hydrocarbons (PAH) in an urban estuary.

2.) Steve Lieberman, Bart Chadwick, Jim Leather (NRaD, San Diego) and I are studying PAH in contamnated sediments of Boston Harbor and San Diego Bay using a time-resolved fluorescence probe (Doctoral Dissertation, Yixian Zhang). We are also interested on the effects of ccontaminated sediments on water quality due to benthic fluxes (Masters Thesis, Gongmin Lei). This project is funded by the DOE Measurement Sciences Program.

3.) Jim Bales (MIT), Bernadette Johnson (MIT Lincoln Labs), John Zayhowski (MIT Lincoln Labs), Bernie Gardner, Carl Gruesz (Masters Thesis) and I developing a low power, miniaturized fluorometer for use on autonomous underwater vehicles (MIT SeaGrant funded).

4.) Dan Repeta, Tim Eglinton, doctoral candidate Lihini Aluwihare (all at WHOI), Doctoral candidate Penny Vlahos (UMassBoston)and I completing a DOE Ocean Margins Program project involving characterizing DOM on the Mid-Atlantic Bight and determining the fluxes of DOC across the continental shelf of the northeast United States.

REFERENCES

none